Application Note 117

Monitoring VOCs in Stationary Source Emissions Using Sorbent Tubes with Analysis by TD-GC/MS in Accordance with Chinese EPA Method HJ 734-2014

Application Note

MARKES international

Abstract

This application note demonstrates the excellent performance offered by Markes International's automated cryogen-free thermal desorption (TD) system for the analysis of volatile organic compounds (VOCs) in stationary source emissions, sampled using sorbent tubes. The system used is compliant with Chinese EPA Method HJ 734-2014, and features automated quantitative re-collection of split flows, which allows repeat analysis, method development, and result verification.

Introduction

Volatile organic compounds (VOCs) are important precursors for atmospheric photochemical reactions, including those that generate low-level ozone and particulate matter that give rise to poor air quality. In addition, some of these VOCs are harmful to health in their own right, and these air toxics or hazardous air pollutants (HAPs) are therefore monitored in many industrial and urban environments. They range in volatility from chloromethane (methyl chloride) and acetone to hexachlorobutadiene and dodecene, and include polar as well as nonpolar compounds. Several national and international standard methods have been developed for air toxics and related applications, including US EPA Methods TO-15 (canisters) and TO-17 (sorbent tubes).

Agilent Technologies

In China, concern over poor air quality led the Chinese Ministry of Environmental Protection (MEP) to request a reduction in VOC emissions as part of the Twelfth Five-Year Plan in 2012. Accordingly, in September 2013, the State Council published the Atmospheric Pollution Control Act in which it outlined a comprehensive plan affecting key industries releasing VOCs. In addition, the MEP also published a number of control standards and methods, including HJ 644-2013 (*Ambient air – Determination of volatile organic compounds – Sorbent adsorption and thermal desorption gas chromatography mass spectrometry method*) and HJ 734-2014 (*Stationary source emission – Determination of volatile organic compounds – Sorbent adsorption and thermal desorption gas chromatography mass spectrometry method*).

In response to demand for measurement of air toxics, analytical technologies have been developed that offer an automated platform compliant with sorbent-tube-based methods. This application note describes the sampling of VOCs in stationary source emissions using sorbent tubes, followed by HJ 734-compliant analysis using an automated, cryogen-free thermal desorption-gas chromatography-mass spectrometry (TD-GC/MS) system.

Background of thermal desorption

Thermal desorption (TD) is a versatile GC preconcentration technology that is used to analyze volatile and semivolatile organic compounds (VOCs and SVOCs) in a wide range of sample types. By concentrating organic vapors from a sample into a very small volume of carrier gas (Figure 1), TD maximizes sensitivity for trace-level target compounds, helps to minimize interferences, and routinely allows analyte detection at the ppb level or below. It also greatly improves sample throughput by allowing full automation of sample preparation, desorption/extraction, preconcentration, and GC injection.

The 'xr' range of TD instruments from Markes International enhances these capabilities, offering a wide analyte range (C_2-C_{44} including reactive species), automated re-collection and reanalysis of split portions for method validation and compliance with standard methods, optional internal standard addition for improved confidence in results, and electronic/manual options for control of carrier gas. This study used a TD100-xr for fully automated analysis of up to 100 sorbent tube samples.

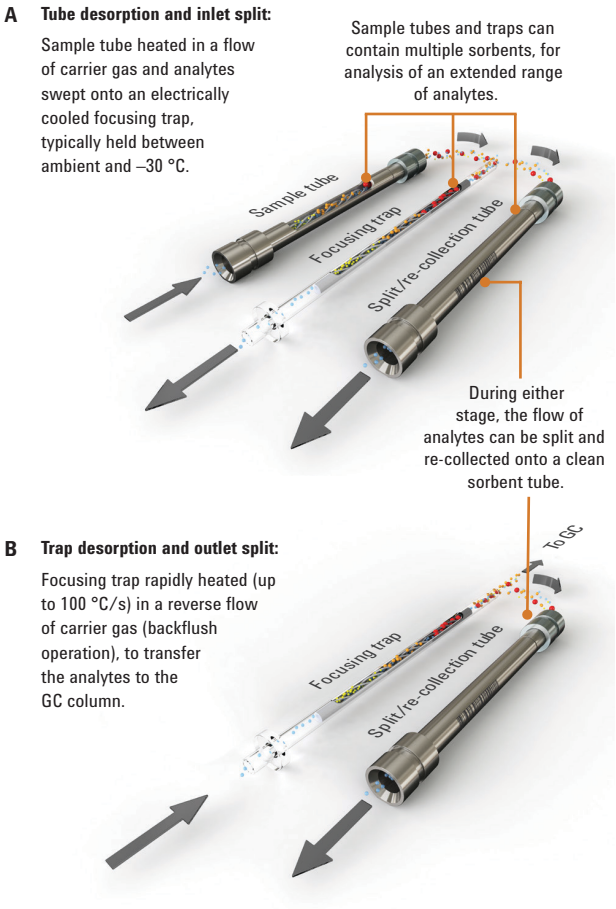


Figure 1. How two-stage thermal desorption works.

Experimental

Standards

This investigation used (a) 1 mL of the HJ 734 standard solution, containing 22 target compounds at 2,000 mg/L in methanol, and (b) an internal standard containing (trifluoromethyl)benzene and bromofluorobenzene at 2,500 mg/L in methanol. The standard solution was diluted to 5, 10, 20, 50, and 100 µg/mL, and the internal standard solution was diluted to 50 µg/mL.

All sorbent tubes were conditioned in a stream of nitrogen using a Markes TC-20 multitube conditioning unit. A 1 µL sample of each standard solution and 1 µL of the internal standard were loaded onto a sorbent tube in a stream of nitrogen using the Calibration Solution Loading Rig (Markes International), giving loadings of target compounds of 5, 10, 20, 50, and 100 ng, respectively. These masses are equivalent to mixing ratios of 4.2, 8.3, 16.7, 41.7, and 83.3 ppbv for a 300 mL air volume.

Table 1. Instrumental parameters.

Parameter	Value
Real air sample	
Sampling:	ACTI-VOC low-flow pump (Markes International) in constant-flow mode (±5%)
Flow rate:	50 mL/min for 6 minutes (total volume 300 mL). For high-temperature, high-humidity samples, the sorbent tube temperature should not be less than the ambient air temperature, to prevent condensation.
TD	
Instrument:	TD100-xr (Markes International)
Tube:	Universal (Markes International part no. C3-AXXX-5266)
Trap:	Air toxics (Markes International part no. U-T15ATA-2S)
Tube dry-purge:	1.0 minute at 60 mL/min
Tube desorb:	300 °C (5 minutes)
IS flow:	10 mL/min
Trap low:	25 °C. Although HJ 734 states a trap low of –10 °C, the air toxics trap used allows a wide range of compounds (down to C_3) to be trapped at ambient temperature without retaining excess water. This higher trap temperature avoids problems caused by ice, improving system stability.
Trap heating rate:	Max
Trap high:	250 °C (3 minutes)
Outlet split:	10 mL/min
Split ratio:	7.7:1
TD flow path temperature:	120 °C
GC	
Carrier gas:	Helium
GC column:	Agilent DB-1, 30 m × 0.25 mm, 1.0 µm, or Agilent DB-624, 60 m × 0.32 mm, 1.4 µm
Mode:	Constant-flow, 1.5 mL/min
Oven ramp:	**DB-1 column:** 35 °C (3 minutes), then 15 °C/min to 85 °C (0 minutes), then 25 °C/min to 220 °C (1 minute) To improve the sensitivity and efficiency of the analysis, the temperature ramp program suggested in HJ 734 was modified to improve peak shape and reduce the analysis time from 30 minutes to 12 minutes. **DB-624 column:** 40 °C (8 minutes), then 8 °C/min to 240 °C (3 minutes)
MS	
Ion source:	250 °C
Transfer line:	230 °C
Full scan range:	*m/z* 36-180 (0-2.2 minutes), *m/z* 33-270 (2.2+ minutes)

Results and Discussion

Chromatography

Figure 2A shows the chromatogram obtained for a standard sample with 100 ng of each target compound on-tube, which is equivalent to the amount in 300 mL of air at 83 ppb per analyte. Excellent peak shape was obtained for all analytes, as illustrated for the challenging polar compound isopropanol (Figure 2B) and a group of later-eluting compounds (Figure 2C). Note that the steep GC temperature ramp used increases productivity and improves peak shape, but does not negatively affect the separation of these compounds. Rapid desorption of the focusing trap in the TD instrument also helps to ensure sharp peaks, and this performance is maintained even with splitless analysis, ensuring optimum sensitivity for trace-level analytes.

In addition to the Agilent DB-1 column suggested in HJ 734, an Agilent DB-624 column was also used to separate these compounds (Figure 3). This column is cited in Chinese EPA Method HJ 644 for the analysis of air toxics in ambient air, and so use of this column would allow a laboratory to work on HJ 734 and HJ 644 applications without changing GC configuration.

Use of high split ratios for concentrated samples

For high-concentration samples (for example, source emissions with analytes at 100-1,000 µg/mL), a higher split ratio should be used to reduce the risk of detector contamination. To assess the performance of this protocol, 1 µL of a 1,000 µg/mL standard solution was loaded onto a sorbent tube, and analyzed with an outlet split flow of 48 mL/min, giving an outlet split ratio of 33:1 (Figure 4). A reanalysis of the same tube shows minimal carryover (<0.5%), even with this high-concentration sample.

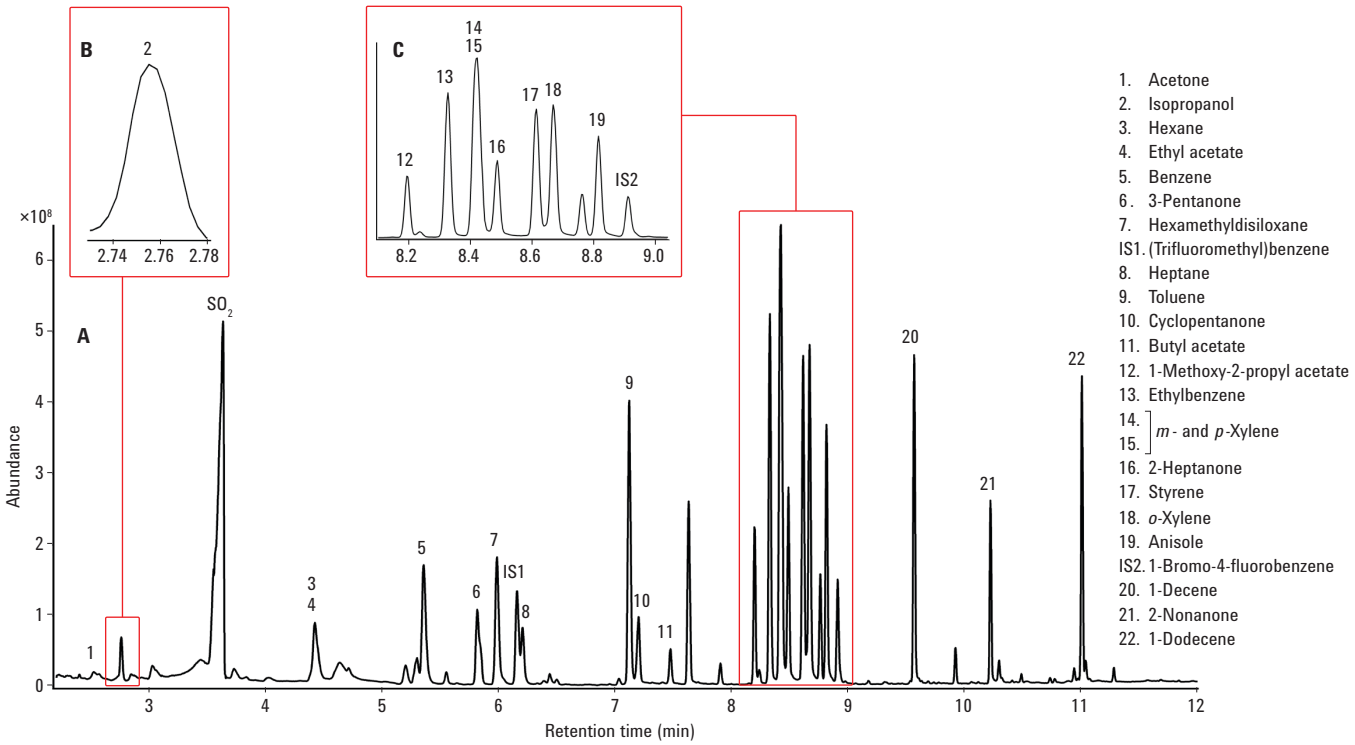


Figure 2. A) Analysis of the HJ 734 standard at 100 ng on-tube per analyte, equivalent to 300 mL of air at 80 ppbv. The 22 target compounds cited in the method are labeled. B) Expansion of the peak for isopropanol, showing excellent peak shape. C) Expansion of peaks 12-19, showing excellent peak shape and good separation.

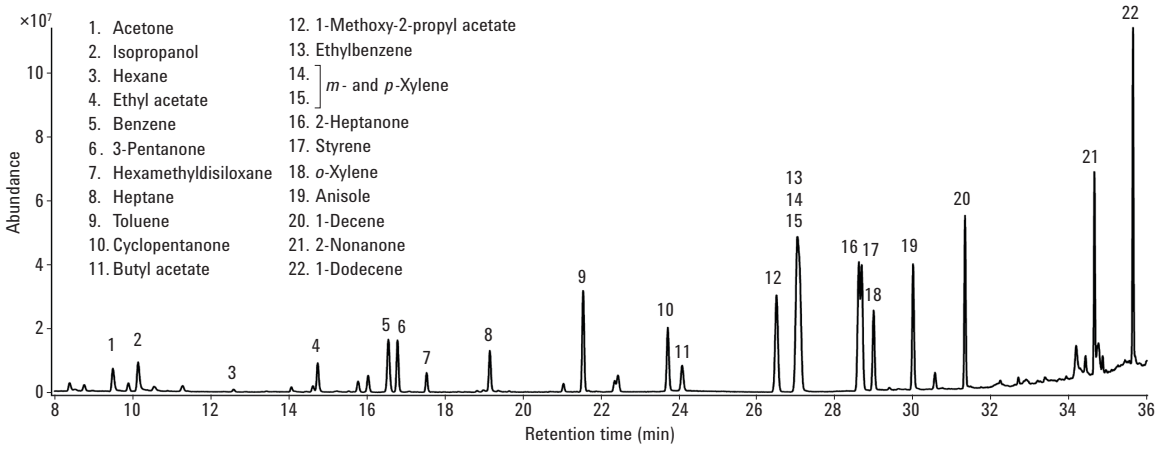
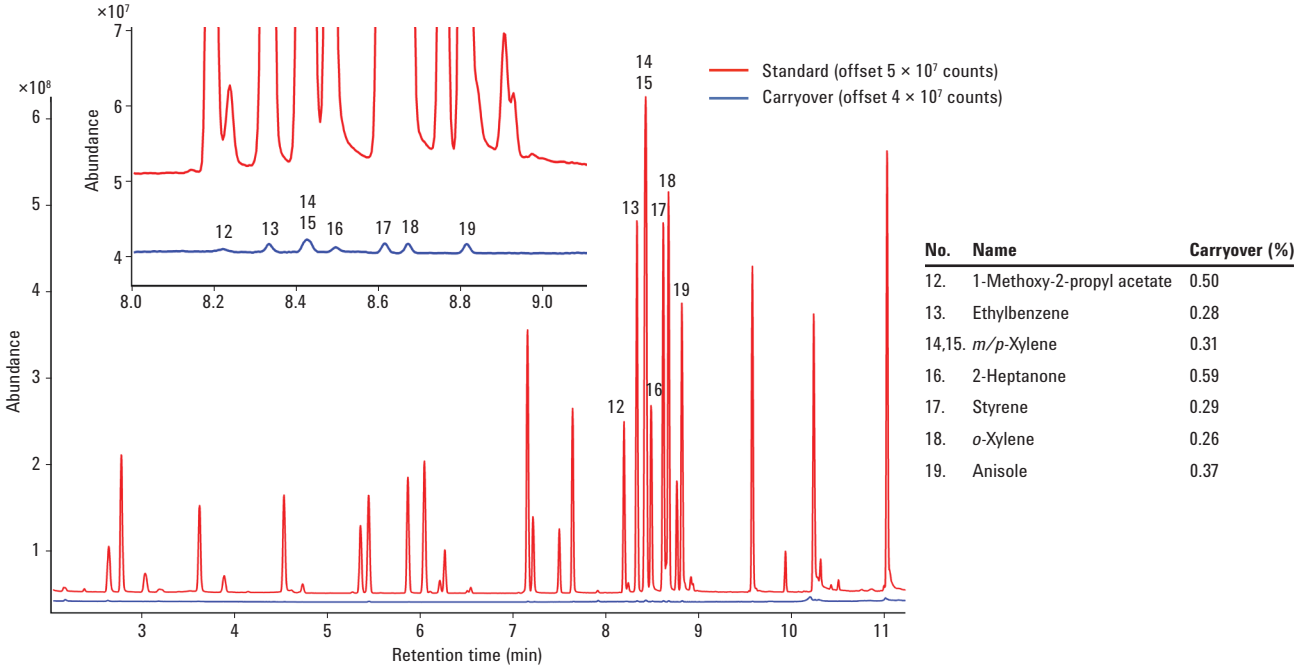


Figure 3. Analysis of an HJ 734 standard at 20 µg/mL with a 4.3:1 split ratio using an Agilent DB-624 column, which is also applicable to the analysis of air toxics, in accordance with HJ 644.



No.	Name	Carryover (%)
12.	1-Methoxy-2-propyl acetate	0.50
13.	Ethylbenzene	0.28
14,15.	*m/p*-Xylene	0.31
16.	2-Heptanone	0.59
17.	Styrene	0.29
18.	*o*-Xylene	0.26
19.	Anisole	0.37

Figure 4. Red trace: Analysis of a 1 µL of a 1,000 µg/mL standard, equivalent to 300 mL of air at 833 ppbv. Blue trace: Repeat analysis of the same tube, showing minimal carryover. The inset shows an expansion of the group of compounds eluting between 8 and 9 minutes.

Linearity

System linearity was assessed by analysis of standard solutions at 5-100 µg/mL (equivalent to analyte concentrations of 4.13, 8.25, 16.50, 41.25, and 82.55 ppbv with a 300 mL sample volume), which is consistent with the actual sample concentrations from typical emission sources.

Excellent linearity (R^2 >0.99) was obtained for all analytes (Table 2), and Figure 5 shows the results for seven compounds, covering the volatility and polarity ranges in the target compound list.

Reproducibility and limits of detection

Eight repeat analyses of 1 µL of a 5 µg/mL standard (equivalent to 4.2 ppbv in a 300 mL air sample) were conducted, and showed excellent consistency of retention time and peak area (Table 2). Retention time RSDs for all compounds were less than 0.1%, peak area RSDs were below 8%, and limits of detection (LODs) ranged 0.002-0.016 µg/mL.

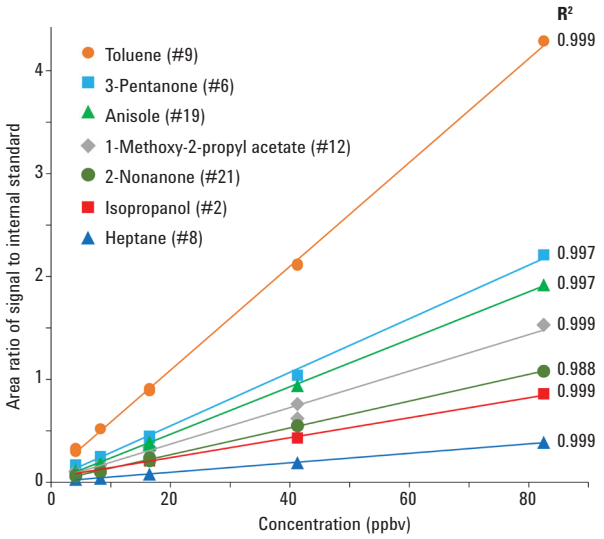


Figure 5. Linearity plots for seven example compounds cited in HJ 734, at levels equivalent to 4-83 ppbv in a 300 mL air sample.

Table 2. Results for analysis of the 22 target compounds in accordance with HJ 734.

					RSD (%) (n = 5)		
No.	Name	t_R (min)	Quant ion (*m/z*)	Linearity (R^2)	t_R	Peak area	MDL (mg/m³)
1	Acetone	2.46	58	0.996	0.180	5.9	0.013
2	Isopropanol	2.72	45	0.999	0.118	5.8	0.005
3	Hexane	4.39	41	0.994	0.058	3.5	0.016
4	Ethyl acetate	4.43	43	0.998	0.086	5.0	0.004
5	Benzene	5.31	78	0.998	0.059	4.4	0.004
6	3-Pentanone	5.82	57	0.997	0.041	2.2	0.002
7	Hexamethyldisiloxane	5.96	147	0.996	0.050	5.6	0.003
IS1	(Trifluoromethyl)benzene	6.13	146	—	0.049	3.4	—
8	Heptane	6.18	43	0.999	0.047	6.3	0.004
9	Toluene	7.10	91	0.999	0.048	4.2	0.003
10	Cyclopentanone	7.19	55	0.998	0.041	3.8	0.002
11	Butyl acetate	7.63	43	0.999	0.039	2.4	0.002
12	1-Methoxy-2-propyl acetate	8.18	43	0.999	0.046	2.8	0.002
13	Ethylbenzene	8.31	91	0.998	0.053	2.9	0.002
14,15	*m-/p*-Xylene	8.40	91	0.998	0.044	2.7	0.002
16	2-Heptanone	8.47	43	0.998	0.040	4.1	0.003
17	Styrene	8.60	104	0.999	0.034	4.0	0.003
18	*o*-Xylene	8.65	91	0.996	0.042	2.9	0.002
19	Anisole	8.80	108	0.997	0.042	3.1	0.002
IS2	1-Bromo-4-fluorobenzene	8.89	95	—	0.030	5.0	—
20	1-Decene	9.55	41	0.997	0.029	4.5	0.004
21	2-Nonanone	10.21	58	0.988	0.024	8.0	0.005
22	1-Dodecene	11.00	69	0.996	0.027	3.5	0.003

Quantitative re-collection of split flows

Markes' TD instruments have the ability to re-collect samples by directing the split flow (which would otherwise carry excess sample to vent) onto a sorbent tube. This process of re-collection can either be onto the tube from which the sample was originally desorbed, or onto a clean tube. This process can be fully automated, and offers a significant advantage over solvent extraction, because it allows a single sample to be analyzed multiple times. Sample splitting and re-collection makes method validation easier, and more importantly, avoids the need to collect another sample should the analysis unexpectedly fail to proceed correctly.

Figure 6 shows a repeat analysis of 100 ng standard with a 7.7:1 split flow, illustrating quantitative re-collection over a wide range of volatilities. As expected, the re-collected sample is slightly less abundant than the original due to the 8:1 split, and the accuracy of the splitting/re-collection process was verified by performing seven re-collection/analysis cycles with the same split ratio. This showed excellent consistency with the theoretical values (Figure 7).

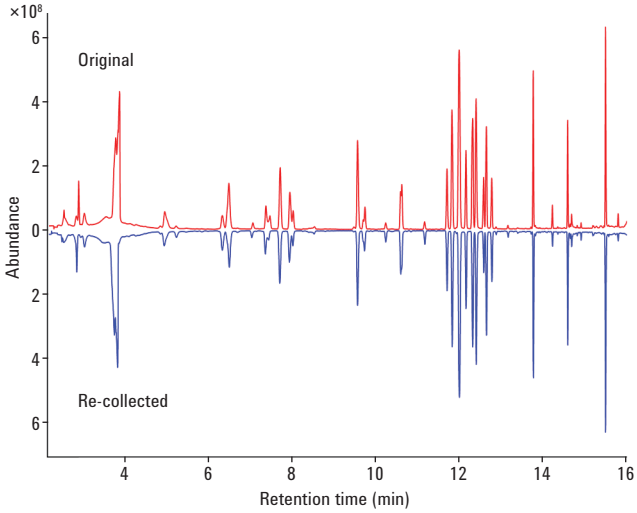


Figure 6. Original analysis (red) and repeat analysis (blue) of tubes containing analyte masses equivalent to 83 ppbv in a 300 mL sampling volume, analyzed with a 7.7:1 outlet split.

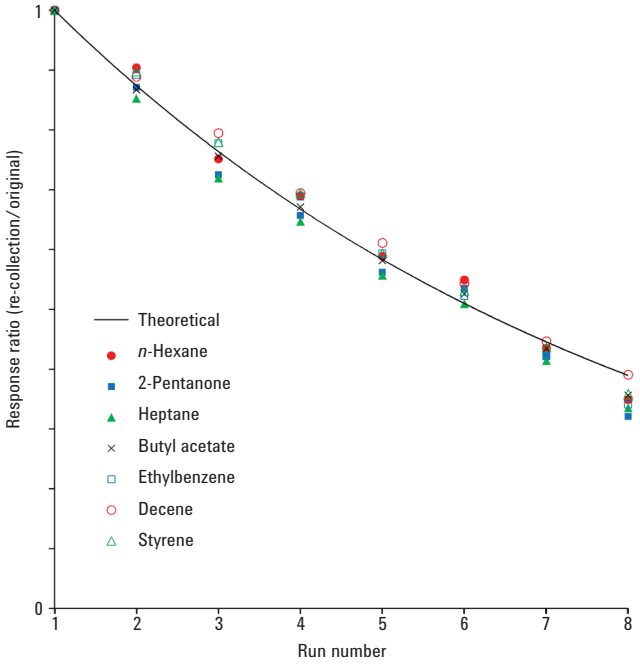


Figure 7. Evaluation of the decay in responses for seven key compounds from a tube repeatedly analyzed with a 7.7:1 outlet split.

Real air sample

To evaluate the performance of the system for a real-world scenario, 300 mL of air from the exhaust of a restaurant was taken during a busy lunchtime period. The sample was analyzed using a DB-1 column under the conditions described earlier, with an outlet split of 7.7:1. The results show the detection of a range of HJ 734 target compounds, even those at trace levels (Figure 8).

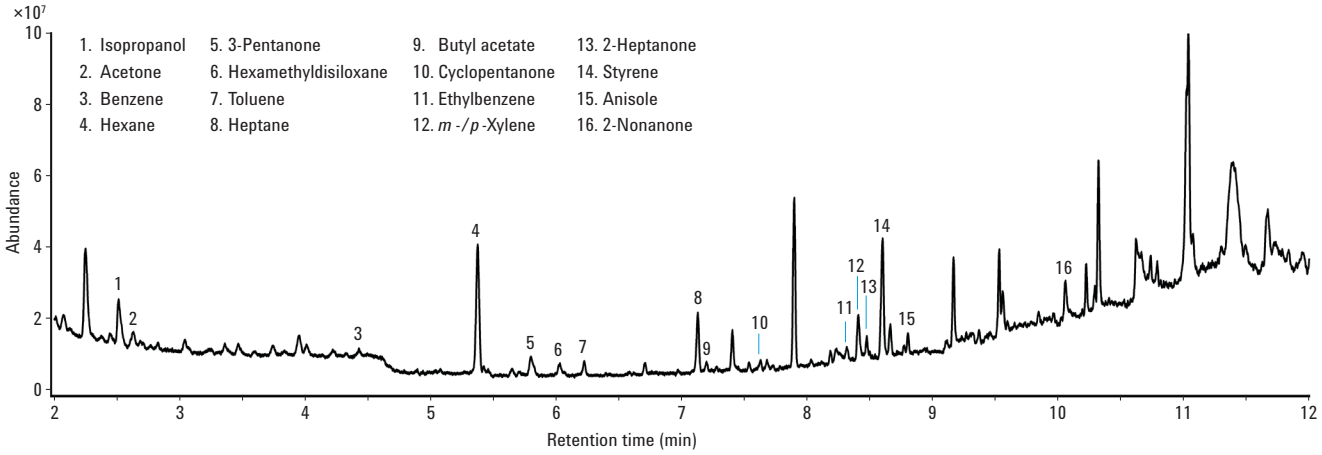


Figure 8. Analysis of air from the exhaust of a restaurant during a busy lunchtime. Peaks labeled are those cited in HJ 734.

Conclusions

This application note demonstrates that Markes International's automated, cryogen-free, thermal desorption systems offer excellent results for monitoring priority pollutants in source emissions in accordance with Chinese EPA Method HJ 734. A particular feature of this method is the automated quantitative re-collection of split flows offered by the thermal desorption instrument, which makes method development and validation of results straightforward.

Trademarks

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Applications were performed under the stated analytical conditions. Operation under different conditions, or with incompatible sample matrices, may impact the performance shown.

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